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# A Method for Predicting Service Life of Zinc Rich Primers on Carbon Steel

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# **A Method for Predicting Service Life of Zinc Rich Primers on Carbon Steel**

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April 1986

## PREDICTING SERVICE LIFE OF ZINC RICH PRIMERS

Zinc rich primers are used at the Kennedy Space Center (KSC) to protect the steel launch structures from the Florida coastal beach environment to which they are exposed. Because of the importance of minimizing the down time of the launch structures and reducing the maintenance costs, it is critical that only the best zinc rich primers be used on these structures. For this reason KSC has had an active evaluation program of zinc rich primers for over 20 years and has observed that the primers vary widely in their ability to protect iron test panels. The test program consists of first evaluating the application characteristics of each primer and then exposing those primers passing the application qualifications to the marine environment at the KSC Beach Corrosion Test Site. The coatings, which are applied to KTA (Tator) test panels, are evaluated against ASTM D-610 rust grades after 18 months exposure in the basic qualification test and periodically after the next several years. The better zinc rich primers will earn a grade of 10 after 5 years whereas the poorest primers will show major rusting (Rust Grade 1) after only 18 months. Although the data collected accurately portrays the effectiveness of a primer, it is a long process in that 5 years is required for a firm characterization of the primer. For this reason, a quick laboratory screening test method which would provide predictions of life expectancy

equivalent to 5 year beach exposure ratings was desired. This paper describes a test method which appears to provide quantitative data relating the chemical availability of zinc in the film with the life expectancy of the primer, as determined from marine beach exposure testing.

### CONCEPT

Zinc based primers are effective, primarily on the basis that zinc has the ability to protect iron through a cathodic protection effect. Assuming that the effectiveness of the primer is a function of the availability of zinc to participate in the protection reaction, then the more available the zinc, the greater the protection potential. The method to determine this "availability" of zinc in the primers is based on the following reaction.



In practice, a 1"x3" glass microscope slide was frosted by sand blasting, dipped in the primer, and after drying, partially coated with paraffin so that one square inch of paint was exposed on each side of the slide. This sample was then placed in a solution of cupric sulfate and the decrease in cupric ion content of the solution determined by measuring the light absorption at 700nm after various periods.

This zinc availability test was used to evaluate several primers currently available for which marine beach exposure data was available from previous programs. Results were evaluated and a correlation between zinc availability and ASTM rust grade was shown.

#### EXPERIMENTAL:

A 0.244M  $\text{CuSO}_4$  stock solution was prepared by dissolving 15.2g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 250ml of water. This yielded a solution with an absorbance of 1.615 @ 700nm and a Cu content of 0.2875g/absorbance unit.

The primer sample was prepared by either dipping or spraying the coating to a minimum thickness of 3 mils on a frosted (sand blasted) 1" x 3" microscope slide. After the primer had cured for approximately 72 hours at a temperature of about 24°C and a relative humidity of 50%, the bottom one inch of the slide was marked off on both sides with a felt tip pen and the rest of the slide was "painted" with paraffin wax so that a 1 square inch surface area on each side of the slide would be exposed to the test solution.

Thirty milliliters of the cupric sulfate stock solution at 24°C was then pipetted into a 30ml tall form beaker and the solution stirred at 100 RPM using a small magnetic stirring bar.

A large hose clamp was used to suspend the glass slide in the beaker just above the stirring bar.

After immersion of the slide in the  $\text{CuSO}_4$  solution, the absorbance at 700nm was measured at five minute intervals between 5 and 30 minutes and once more after 60 minutes to characterize the copper/zinc reaction.

Measurements were made by filling a 10mm spectrophotometric cell with liquid removed from the reaction beaker with a medicine dropper. After the absorbance measurement was made at 700nm, the liquid in the cell was returned to its respective beaker.

Zinc availability was calculated using the following equation:

$$(\text{ABS}_0 - \text{ABS}_{15}) * A * B * 1000 = \text{mg of Zinc}$$

where  $\text{ABS}_0$  = initial absorbance of solution at 700nm.

$\text{ABS}_{15}$  = absorbance after 15 minutes.

A = grams of copper per absorbance unit.

B = GMWt Zn / GMWt Cu

The 72 hour curing period was selected after reviewing manufacturers literature. To verify this selection, duplicate samples of primer KK (2 part inorganic) were cured for varying times at either 50% or 100% relative humidity at a temperature of about 24°C. The zinc availability was then measured after 15 minutes exposure in the copper sulfate solution.

Results of this testing are presented in Table 1.

TABLE 1  
EFFECT OF CURING TIME/HUMIDITY ON ZINC AVAILABILITY  
(PRIMER KK)

<u>HOURS CURED</u>	<u>ZINC (mg)</u>	
	<u>50% RH</u>	<u>100% RH</u>
48	92	101
72	96	98
96	92	100
192	93	-

This data shows that the 72 hour cure period is sufficient and that control of humidity is more important than time during curing.

To determine the effect of film thickness on "zinc availability" results, three samples of primer E were tested. Sample E1 had a film thickness of about 3 mils; sample E2, 3.5 mils; and sample E3, 13 mils. Results showed good method reproducibility and also the effect of coating thickness. The results are shown in Table 2 and graphed in Figure 1.

# EFFECT OF COATING THICKNESS

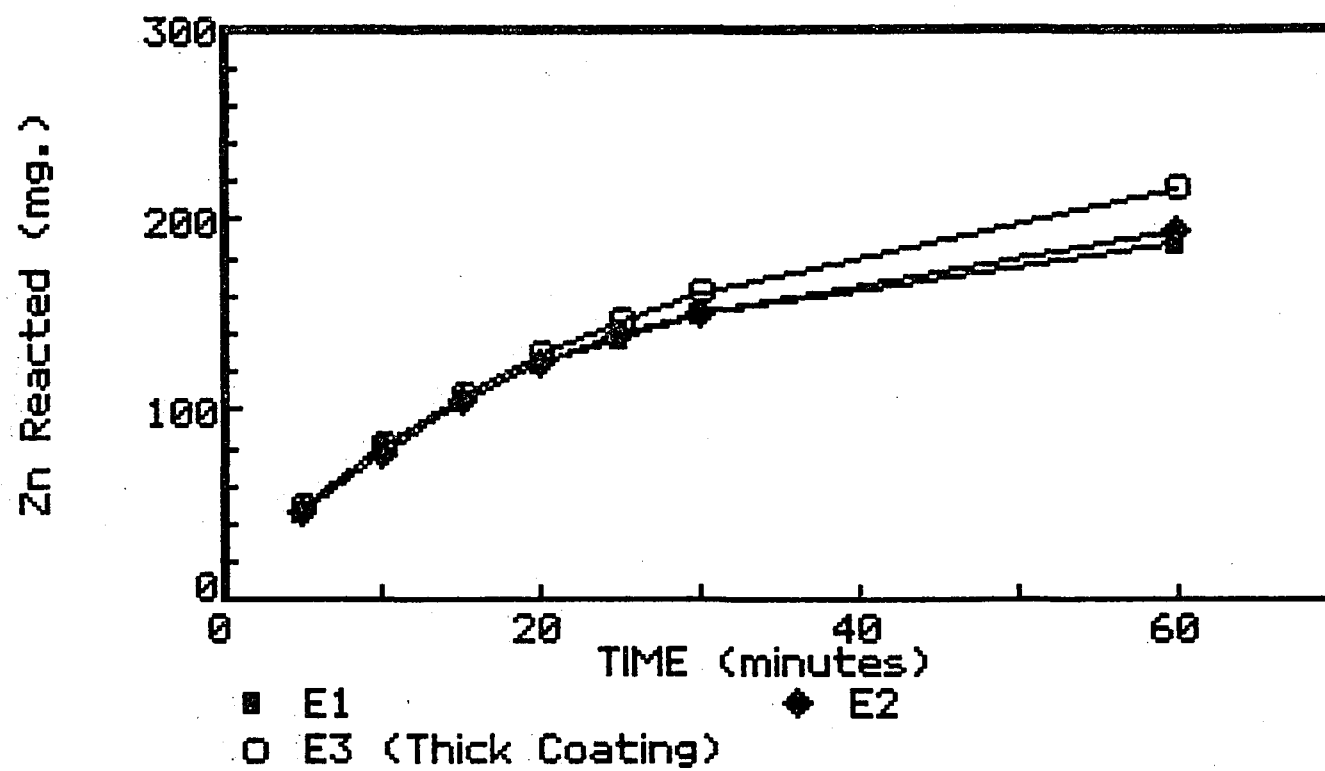


FIGURE 1



TABLE 2  
EFFECT OF COATING THICKNESS ON Zn AVAILABILITY

<u>TIME(min)</u>	<u>ABSORBANCE VALUE/(mg Zn)</u>		
	<u>SAMPLE-E1</u>	<u>SAMPLE-E2</u>	<u>SAMPLE E3</u>
5	1.457 (47)	1.461 (46)	1.448 (49)
10	1.341 (81)	1.352 (78)	1.339 (82)
15	1.258 (106)	1.261 (105)	1.250 (108)
20	1.197 (124)	1.194 (124)	1.179 (129)
25	1.148 (138)	1.143 (140)	1.120 (146)
30	1.109 (150)	1.104 (151)	1.072 (161)
60	0.979 (188)	0.957 (195)	0.885 (216)
1440	0.8(*) (241)	0.8(*) (241)	0.016*(473)

(\*) Values approximate because of solution evaporation.

The three samples gave good reproducibility for the first 15 minutes and then the effect of film thickness began to appear. Whereas the thin film samples, E1 and E2, leveled off at an absorbance of 0.8; sample E3, the heavy film sample, depleted nearly all ionic Cu in the solution.

Samples of primers which had previously been tested at the KSC marine beach exposure site were obtained from their manufacturers and evaluated for zinc availability. Results are presented in Table 3. It was assumed that the primer formulations had not changed since the original studies were conducted.

TABLE 3

ZINC PRIMERS - ABSORBANCE 700nm vs TIME

<u>PRIMER</u>	<u>5 MIN</u>	<u>10 MIN</u>	<u>15 MIN</u>	<u>20 MIN</u>	<u>25 MIN</u>	<u>30 MIN</u>	<u>60 MIN</u>
A	1.566	1.544	1.531	1.522	1.518	1.510	1.481
B	1.498	1.452	1.427	1.409	1.395	1.385	1.353
C	1.457	1.388	1.335	1.293	1.259	1.231	1.104
D	1.448	1.344	1.277	1.226	1.182	1.145	1.003
E	1.457	1.341	1.258	1.197	1.148	1.109	0.979
F	1.444	1.332	1.253	1.195	1.149	1.108	0.949
G	1.432	1.321	1.243	1.168	1.105	1.074	0.933
H	1.417	1.313	1.225	1.147	1.058	0.995	0.697
I	1.387	1.282	1.212	1.155	1.107	1.070	0.902
J	1.376	1.259	1.182	1.116	1.053	1.006	0.778
K	1.596	1.582	1.574	1.568	1.562	1.560	1.540

## DISCUSSION OF RESULTS

The zinc availability for the primers tested was calculated and is shown in Table 4.

TABLE 4

ZINC AVAILABILITY VALUES FOR VARIOUS PRIMERS

<u>PRIMER</u>	<u>ABSORBANCE</u> <u>@ 700nm</u>	<u>Zn</u> <u>(mg)</u>
A (1-part organic)	1.531	24.8
B (1-part inorganic)	1.427	55.6
C (1-part inorganic)	1.335	82.8
D (1-part inorganic)	1.277	100.0
E (2-part inorganic)	1.258	105.6
F (2-part inorganic)	1.253	107.1
G (2-part inorganic)	1.243	110.0
H (2-part inorganic)	1.225	115.4
I (1-part inorganic)	1.212	119.2
J (2-part inorganic)	1.182	128.1
K (2-part inorganic)	1.574	12.2

The difference between the zinc reactivity of poor and excellent primers is shown graphically in Figure 2 where 4 representative primers are plotted. The poorer primers reacted slowly in the

# TYPICAL ABSORBANCE vs TIME CURVES

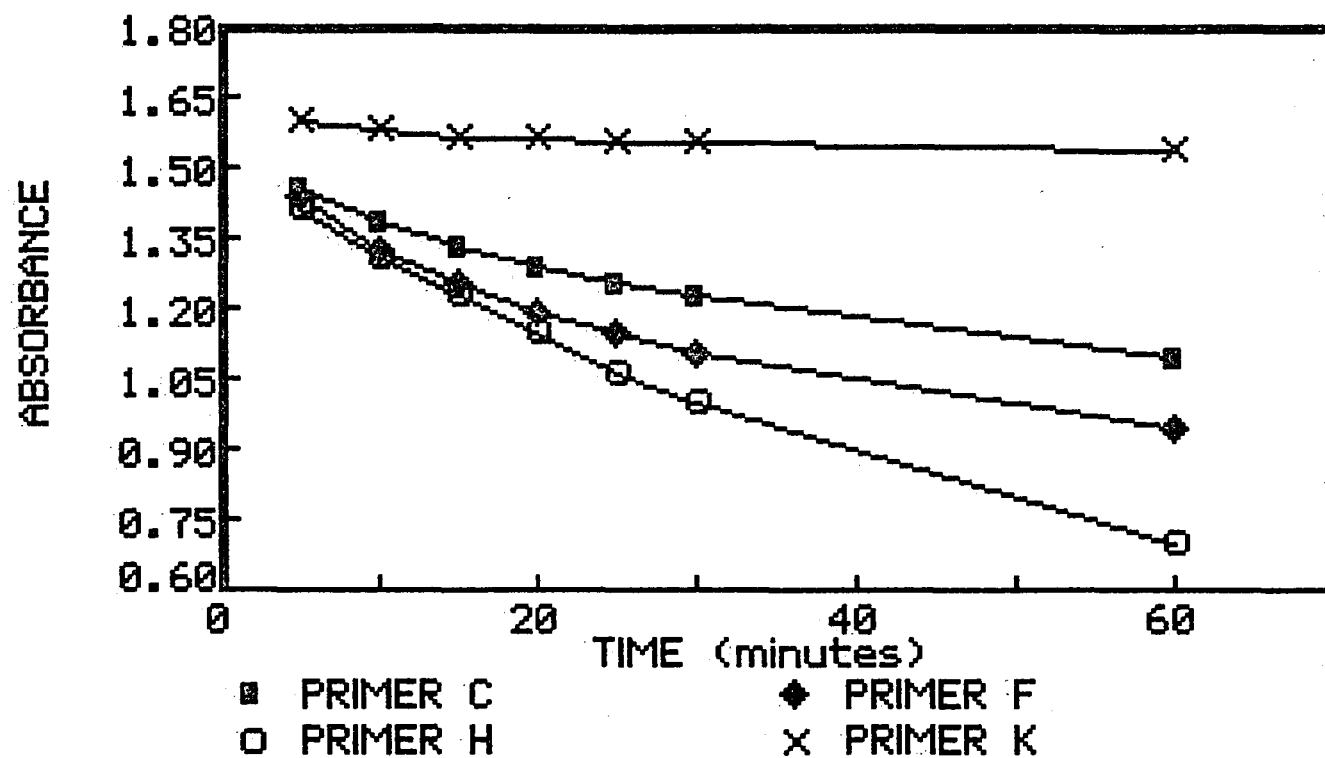


FIGURE 2

ionic copper solution, whereas the better primers reacted quickly and released much more zinc. Plotting this data with absorbance versus log of time showed a linear relationship between 15 and up to 60 minutes. The upper time limit was dependent on the thickness of the primer on the slide. Thicker coatings extended the linear portion of the curve.

The amount of zinc that reacted in 15 minutes was chosen as the key value to characterize the coatings. This time was selected because it was long enough to show any difference between the primers, but short enough to be unaffected by the film thicknesses used in this study (minimum of 3 mils). Zinc values were derived from photometrically determined copper concentrations.

Figure 3 shows the relationship between quantity of zinc reacted and the ASTM rust grade after various periods of marine beach exposure. A is a one part organic based zinc rich primer. B,C,D and I are one part inorganic based zinc primers and the remainder are two part inorganic based zinc rich primers.

All primers with less than 100mg of zinc available showed some rust after only 18 months and degraded significantly after 36 months exposure. Primers with zinc availability levels higher than 105 mg showed less than .01% rust after 60 months of exposure. Taken at face value, these data indicate that any

ASTM RUST GRADE

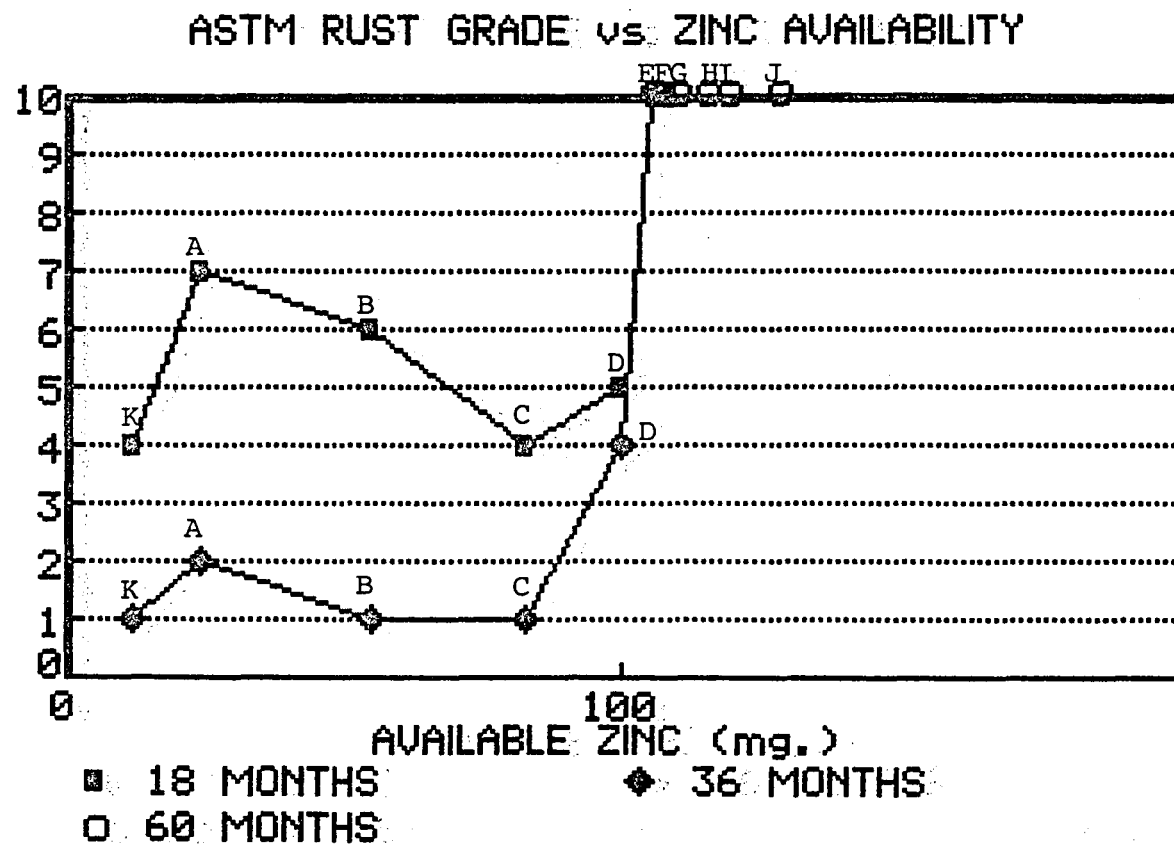


FIGURE 3

primer with a zinc availability level of higher than 105 mg is going to last at least five years and any primer with a lower value will fail within 18 months. Failure, in this context being an ASTM rust grade of less than 9.

The threshold nature of the curve is intriguing. Indications are that a minimum quantity of available zinc is necessary to provide long term protection and that there are only "good" and "bad" primers. The general decrease in ASTM Rust Grade values with increasing zinc availability up to the threshold is also of interest. It is theorized that adding zinc to an otherwise good barrier coating decreases the barrier coatings effectiveness without adding any cathodic protection until a critical level is obtained, perhaps due to zinc particle to particle contact, at which point the primer becomes a cathodic protector.

It would also be of interest to measure the electrical conductivity of these coatings to determine if metal to metal contact is occurring at the zinc availability threshold.

Also of interest is the fact that a two part inorganic primer had the dubious distinction of having the lowest zinc availability and a one component primer had one of the highest ratings.

#### FUTURE STUDIES:

Twenty-one two part inorganic zinc rich primers are going to be exposed for 60 months at the Kennedy Space Center beach

exposure site beginning in the winter of 1985. These primers will be evaluated at the end of 18, 36 and 60 months.

These 21 primers were evaluated by the zinc availability test. The results are presented in Table 5. These predictions are based on the results graphed in figure 3. An interim report will be issued after the 18 month exposure period. This study should either confirm or disprove the validity of the screening method.

Electrical conductivity and scanning electron microscope research will be conducted in an attempt to find the physical or chemical difference between the "good" and "bad" primers.



TABLE 5

## PREDICTED ASTM RUST GRADE BASED ON ZINC AVAILABILITY

<u>PRIMER</u>	ZINC AVAILABILITY <u>(mg)</u>	PREDICTED RUST GRADE <u>AFTER 18 MONTHS</u>
AA	124	10
BB	111	10
CC	106	10
DD	74	<8
EE	89	<8
FF	128	10
GG	120	10
HH	98	<8
II	107	10
JJ	110	10
KK	101	<8
LL	72	<8
MM	124	10
NN	137	10
OO	72	<8
PP	112	10
QQ	88	<8
RR	59	<8
SS	129	10
TT	106	<8
UU	89	<8
VV	89	<8

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